

# Application of Principal Component Analysis to Aerosol Mass Spectrometry Data from the Whistler High Elevation Site



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## INTRODUCTION

As part of the INTEX-B project a Time of Flight Aerosol mass Spectrometer (ToF-AMS, Aerodyne Research Inc.) was deployed at the peak of Whistler Mountain (2182 mASL), to examine the effect of trans-pacific transport, as well as local and regional pollution influences on the site. The Whistler mountain site (BC, Canada), is an ideal location for studying these processes as it is often influenced by air masses from the Pacific in the free troposphere.

In order to decipher the complicated particle mass spectra obtained from the ToF-AMS, a Principal Component Analysis (PCA) technique was developed and applied to the data. Results of the PCA are presented, which aid in the apportionment of air masses to specific processes, by identifying co-varying aerosol components.

## EXPERIMENTAL

### ToF-AMS Instrument Details

- ☆ Provides particle mass spectra with high time resolution (5 min @ Whistler)
- ☆ Quantifies particle sulfate, nitrate, ammonium, and total organic mass (< 1 µm diameter)
- ☆ size segregated mass distribution for every m/z, high mass range (~800 amu)
- ☆ Alternated between two modes of operation:
  - V-mode: High sensitivity, > unit mass resolution
  - W-mode: Lower sensitivity, high mass resolution (~5000 vs 20 for the Q-AMS)
- ☆ April 19 – May 16, ~66% data recovery



Figure 1. View of the Whistler high elevation site

### Principal Component Analysis (PCA)

- ☆ PCA is a statistical method to reduce the dimensionality of a data set while explaining a maximum of the variance
- ☆ Original Data Matrix (D) contains  $r$  rows, and  $c$  columns:

$$D = \begin{matrix} & m/z & & \\ \text{Sample Time} & d_{11} & d_{12} & d_{13} & \dots & d_{1c} \\ & d_{21} & d_{22} & d_{23} & \dots & d_{2c} \\ & \vdots & \vdots & \vdots & \ddots & \vdots \\ & d_{r1} & d_{r2} & d_{r3} & \dots & d_{rc} \end{matrix}$$

PCA seeks a solution where each point in  $D$  is a linear sum of  $n$  product terms (components):

$$d_{ik} = \sum_{j=1}^n r_{ij} c_{jk} \quad (i = i^{\text{th}} \text{ row}, k = k^{\text{th}} \text{ column})$$

Thus decomposing the data matrix into 2 matrices:

$$[D]_{r \times c} = [R]_{r \times n} [C]_{n \times c}$$

(Score) (Loading)

☆ **Varimax Rotation** is used to transform the scores and loadings into a physically meaningful result

☆ Multiple linear regression of each m/z signal (M) for a given observation (k) on the predicted signal (S = [R]<sub>rot</sub>) from all components (j) is performed as follows:

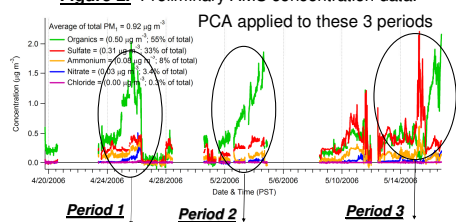
$$M_k = a_0 + \sum_{j=1}^n a_j S_{jk}$$

Repeating this regression for every m/z (1-300) signal results in a relative component profile (a<sub>j</sub>) or mass spectra for each component.

☆ **Component spectra represent common processes not necessarily specific aerosol sources or species, thus a negative contribution is allowed.**

## RESULTS & DISCUSSION

Figure 2. Preliminary AMS concentration data.



Period 3: (below)

- 4 components accounted for >99% of variance

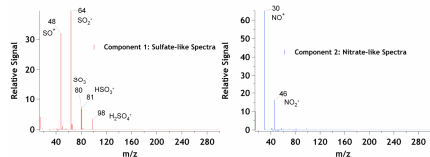


Figure 3. Components 1 and 2 from PCA of period 3.

- ☆ Component 1 spectra is highly similar to the known spectrum of sulfate, with the exception of a few associated organic fragments
- ☆ Component 2 is highly similar to the known spectrum of Nitrate, with several associated organic fragments

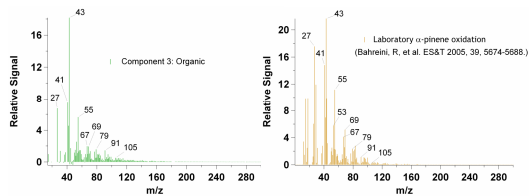


Figure 4. Component 3 from PCA of period 3 and comparison to laboratory generated spectrum

☆ Component 3 is highly similar to the mass spectrum obtained during the oxidation of α-pinene in smog chamber studies. It is likely that component 3 at Whistler is associated with oxidation products of biogenic origin.

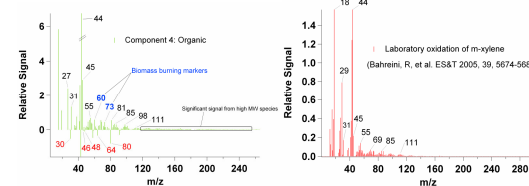
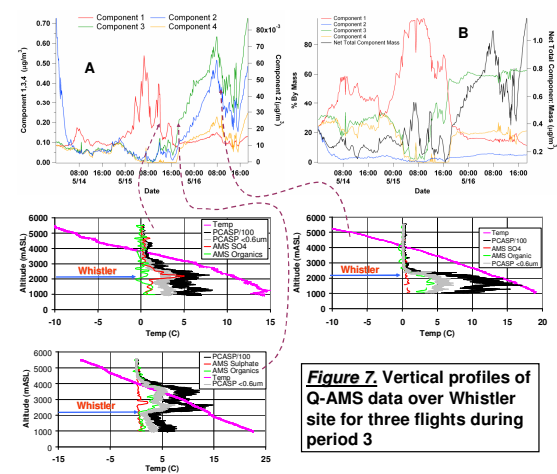


Figure 5. Component 4 from PCA of period 3 and comparison to laboratory generated spectrum

☆ Component 4 is somewhat similar to the m-xylene (anthropogenic) oxidation spectrum. However, significant biomass burning markers are also present (m/z 60, m/z 73 – Levoglucosan). This component is highly oxygenated (m/z 44, 31, 55...) and may also be the result of biomass burning.

☆ Fragments from inorganic species (m/z 30, 46, 64, 80) imply a negative contribution to this component. Possibly a result of meteorology, or chemical processes.

Figure 6. A – PCA derived net mass concentration for each component (Period 3). B – % of net total mass for each component



☆ Component 1 (sulfate) dominates when Whistler is decoupled from the mixed layer, possibly Pacific transport.

☆ Vertical profiles suggest that the high organic mass (biogenic component 3) is a result of subsidence and not linked to valley below.

**Period 1:** (below) - 4 components accounted for >99% of variance with slight differences from components of period 3

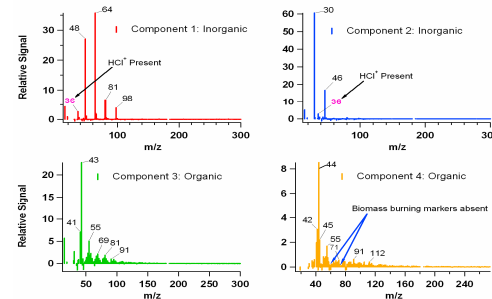


Figure 8. Components derived from the PCA of period 1

☆ Levoglucosan markers (m/z 60, 73) are no longer present in component 4

☆ HCl marker (m/z 36) is evident in the inorganic components (1,2).

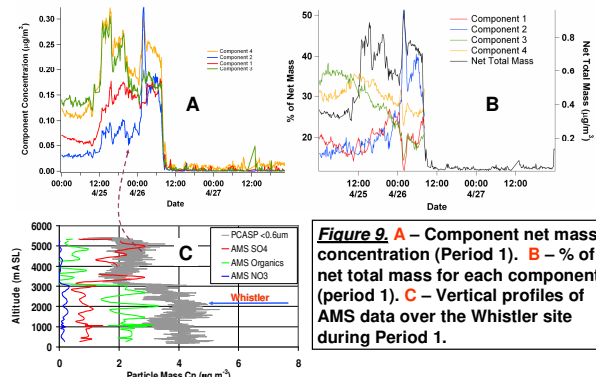


Figure 9. A – Component net mass concentration (Period 1). B – % of net total mass for each component (period 1). C – Vertical profiles of AMS data over the Whistler site during Period 1.

## CONCLUSIONS

- ☆ Four components were usually sufficient to describe the Whistler AMS data, accounting for > 99% of the total variance
- ☆ Biogenic aerosols (component 3) may account for up to 60% of the net total aerosol mass derived by PCA
- ☆ A primarily sulfate component may be a result of trans-Pacific transport
- ☆ Possible biomass burning component was also identified (period 3)
- ☆ Organics during period 3 likely a result of subsidence from aloft
- ☆ Biomass burning was not evident during Period 1
- ☆ HCl was observed in both inorganic components during Period 1
- ☆ Aerosols during period 1 were more likely associated with the valley below (within the boundary layer).

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